1 # Legacy and Emerging Perfluoroalkyl Substances Are Important

2 # Drinking Water Contaminants in the Cape Fear River Watershed of

3 # North Carolina

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30 Abstract

31 Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain

32 PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered

33 perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) occurrence in the Cape Fear River

34 (CFR) watershed, (2) fate in water treatment processes, and (3) adsorbability on powdered

35 activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in

36 raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were

37 high. The US Environmental Protection Agency's lifetime health advisory level (70 ng/L) for

38 perfluorooctane sulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127

39 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean

40 concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was

41 631 ng/L (n=37). Six other PFECAs were detected with three exhibiting chromatographic peak

42 areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation,

43 ozonation, biofiltration, and disinfection was negligible. PFAS adsorbability on PAC increased

44 with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased PFAS

45 affinity for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.

46

47 Introduction

48 Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics,

49 water/stain repellents, firefighting foams and food-contact paper coatings. The widespread

50 occurrence of PFASs in drinking water sources is closely related to the presence of sources such

51 as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.[1]

52 Until 2000, long-chain perfluoroalkyl sulfonic acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$, PFSAs) and

53 perfluoroalkyl carboxylic acids ($C_nF_{2n+1}COOH$, $n \geq 7$, PFCAs) were predominantly used.[2]

54 Accumulating evidence about the ecological persistence and human health effects associated

55 with exposure to long-chain PFASs[3, 4] has led to increased regulatory attention. Recently the U.S.

56 Environmental Protection Agency (USEPA) established a lifetime health advisory level (HAL)

57 of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid

58 (PFOS) concentrations in drinking water.[5, 6] Over the last decade, production of long-chain

59 PFASs has declined in Europe and North America, and manufacturers are moving towards short-

60 chain PFASs and fluorinated alternatives.[7-10] Some fluorinated alternatives were recently

61 identified,[8, 11] but others remain unknown[12-14] because they are either proprietary or

62 manufacturing byproducts.

63 One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was

64 recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing

65 facility.[11] Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-

66 methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-

67 2-propoxypropanoic acid (PFPrOPrA), perfluoro(3,5-dioxahexanoic) acid (PFO2HxA),

68 perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) and perfluoro(3,5,7,9-tetraoxadecanoic) acid

69 (PFO4DA) (Table S1 and Figure S1). The ammonium salt of PFPrOPrA is a known PFOA

70 alternative[15] that has been produced since 2010 with the trade name "GenX". To the knowledge

71 of the authors, the only other published PFECA occurrence data are for PFPrOPrA in Europe and

72 China,[15] and no published data are available on the fate of PFECAs during water treatment.

73 Except for a few studies (most by the manufacturer),[16-20] little is known about the toxicity,

74 pharmacokinetic behavior, or environmental fate and transport of PFECAs.

75 The strong C-F bond makes PFASs refractory to abiotic and biotic degradation,[21] and most water

76 treatment processes are ineffective for legacy PFAS removal.[22-27] Processes capable of removing

77 PFCAs and PFSAs include nanofiltration,[28] reverse osmosis,[25] ion exchange,[28, 29] and activated

78 carbon adsorption,[28, 29] with activated carbon adsorption being the most widely employed

79 treatment option.

80 The objectives of this research were to (1) identify and quantify the presence of legacy PFASs

81 and emerging PFECAs in drinking water sources, (2) assess PFAS removal by conventional and

82 advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) evaluate

83 PFAS adsorbability by powdered activated carbon (PAC).

Materials and Methods

84

85 **Water samples**: Source water of three DWTPs treating surface water in the CFR watershed was

86 sampled between June 14 and December 2, 2013 (Figure S2). Samples were collected from the

87 raw water tap at each DWTP daily as either 8-hour composites (DWTP A, 127 samples) or 24-

88 hour composites (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250-

89 mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a

90 weekly basis. All samples were stored at room temperature until analysis (within 1 week of

91 receipt). PFAS losses during storage were negligible based on results of a 70-day holding study

92 at room temperature. On August 18, 2014, grab samples were collected at DWTP C after each

93 unit process in the treatment train (raw water ozonation, coagulation/flocculation/sedimentation,

94 settled water ozonation, biological activated carbon (BAC) filtration, disinfection by medium

95 pressure UV lamps and free chlorine). Operational conditions of DWTP C on the sampling day

96 are listed in Table S2. Samples were collected in 1-L HDPE bottles and stored at room

97 temperature until analysis. On the same day, grab samples of CFR water were collected in six

98 20-L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing

99 site and stored at 4°C until use in PAC adsorption experiments (background water matrix

100 characteristics in Table S3).

101 **Adsorption experiments**: PFAS adsorption by PAC was studied in batch reactors (amber glass

102 bottles, 0.45 L CFR water). PFECA adsorption was studied at ambient concentrations (~1,000

103 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs ~10-800% of the PFPrOPrA

104 area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water

105 at ~1000 ng/L each. Data from spiked and non-spiked experiments showed that the added legacy

106 PFASs and methanol (1 ppm$_v$) from the primary stock solution did not affect native PFECA

107 removal. A thermally-activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus

108 OH, mean diameter: 12 μm, BET surface area: 1460 m^2/g)[30] proved effective for PFAS removal

109 in a prior study[29] was used at doses of 30, 60 and 100 mg/L. These doses represent the upper

110 feasible end for drinking water treatment. Samples were taken prior to and periodically after

111 PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were negligible.

112 **PFAS analysis:** Information about analytical standards and liquid chromatography-tandem mass

113 spectrometry (LC-MS/MS) methods for PFAS quantification is provided in the supporting

114 information.

Results and Discussion

115

116 **PFAS occurrence in drinking water sources**: Mean PFAS concentrations in source water of

117 three DWTPs treating surface water from the CFR watershed are shown in Figure 1. In

118 communities A and B, only legacy PFASs were detected (mean ∑PFAS: 355 ng/L in community

119 A, 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3.

120 In community A, PFCAs with 4-8 total carbons, perfluorohexane sulfonic acid (PFHxS) and

121 PFOS were detected at mean concentrations >QLs. During the 127-day sampling campaign, the

122 sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The

123 mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L with

124 approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS

125 and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA

126 concentrations were observed in the same area in 2006,[31] suggesting that PFAS source(s)

127 upstream of community A have continued negative impacts on drinking water quality. Also, our

128 data show that legacy PFASs remain as surface water contaminants of concern even though their

129 production was recently phased out in the US. It is important to note, however, that among the

130 PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation

131 shifted from long-chain (~80-85% C$_n$F$_{2n+1}$COOH, n=7-9) in 2006 to short-chain (76%

132 C$_n$F$_{2n+1}$COOH, n=5-6) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both

133 2006 and 2013. Relating total PFAS concentration to average daily stream flow (Figure S4)

134 illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at

135 low flow, consistent with the hypothesis of upstream point source(s).

136

137 In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were

138 most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA

139 and PFOS concentrations were <QL, and the maximum sum concentration of PFOA and PFOS

140 was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be

141 explained by the absence of substantive PFAS sources between the two communities, dilution by

142 tributaries, and the buffering effect of Jordan Lake, a large reservoir located between
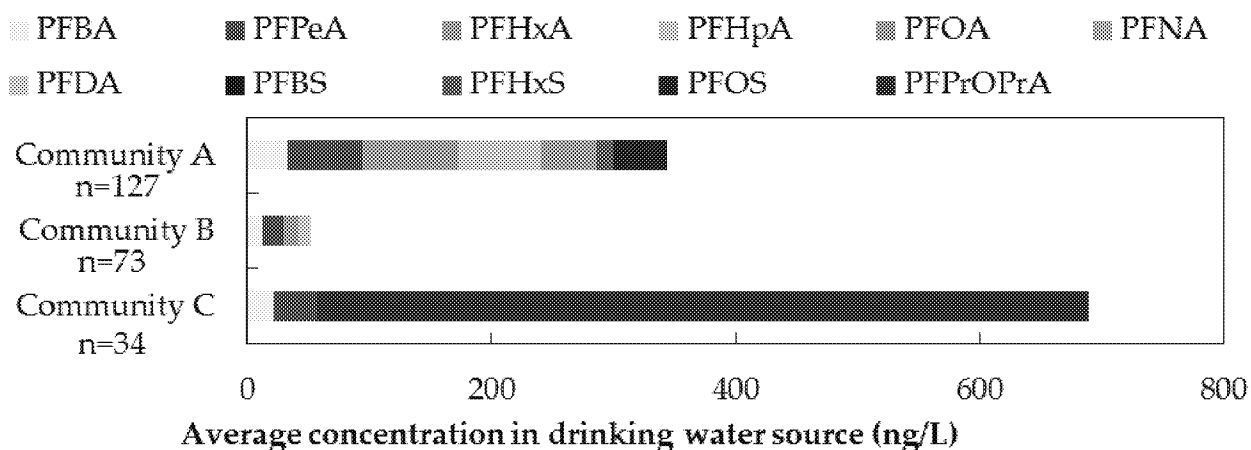
143 communities A and B.

144

Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations

147 represent averages of samples collected between June and December 2013. Individual samples

148 with concentrations < QLs were considered as 0 when calculating averages, and average

149 concentrations < QLs were not plotted.

150

151 In community C (downstream of a PFAS manufacturing site), only mean concentrations of

152 PFBA and PFPeA were >QLs. The relatively low concentrations of legacy PFASs in the finished

153 drinking water of community C are consistent with results from USEPA's third unregulated

154 contaminant monitoring rule for this DWTP.[32] However, high concentrations of PFPrOPrA were

155 detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was

156 approximately eight times the average summed PFCA and PFSA concentrations (79 ng/L). Other

157   PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the

158   highest PFAS concentrations for community C were also observed at low flow (Figure S3).

159   Stream flow data were used in conjunction with PFPrOPrA concentration data to determine

160   PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6

161   to 24 kg/d with a mean of 5.9 kg/d.

162

163   **PFAS fate in conventional and advanced water treatment processes**: To investigate whether

164   PFASs can be removed from impacted source water, samples from DWTP C were collected at

165   the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced

166   treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation,

167   BAC filtration, disinfection by medium pressure UV lamps and free chlorine) did not remove

168   legacy PFASs, consistent with previous studies.[22-26] The data further illustrate that no measurable

169   PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSAs, PFMOPrA,

170   PFPrOPrA and PFMOAA may have increased after ozonation, possibly due to the oxidation of

171   precursor compounds.[25] Disinfection with medium pressure UV lamps and free chlorine (located

172   the between BAC effluent and the finished water) may have decreased concentrations of

173   PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA, but only to a limited extent. Small

174   concentration changes between treatment processes may also be related to temporal changes in

175   source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic

176   residence time of the DWTP.

177   Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was

178   similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in

179   Figure 1; i.e., PFPrOPrA concentrations (400-500 ng/L) greatly exceeded legacy PFAS

180   concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA and PFO3OA) exhibited peak

181   areas 2-113 times greater than that of PFPrOPrA (Figure 2b). The existence of high levels of

182   emerging PFASs suggests a need for their incorporation into routine monitoring.

183

(a)

Concentration of traditional PFASs
at a WTP in Community C (ng/L)

■ PFPrOPrA   PFBA   ■ PFPeA   ▨ PFHxA   ▨ PFHpA   ▨ PFOA

▨ PFNA   ▨ PFDA   ■ PFBS   ■ PFHS   ■ PFOS

(b)

Peak area counts of emerging PFASs
at a WTP in Community C

■ PFPrOPrA   ▨ PFMOAA   ▨ PFMOPrA   ▨ PFMOBA
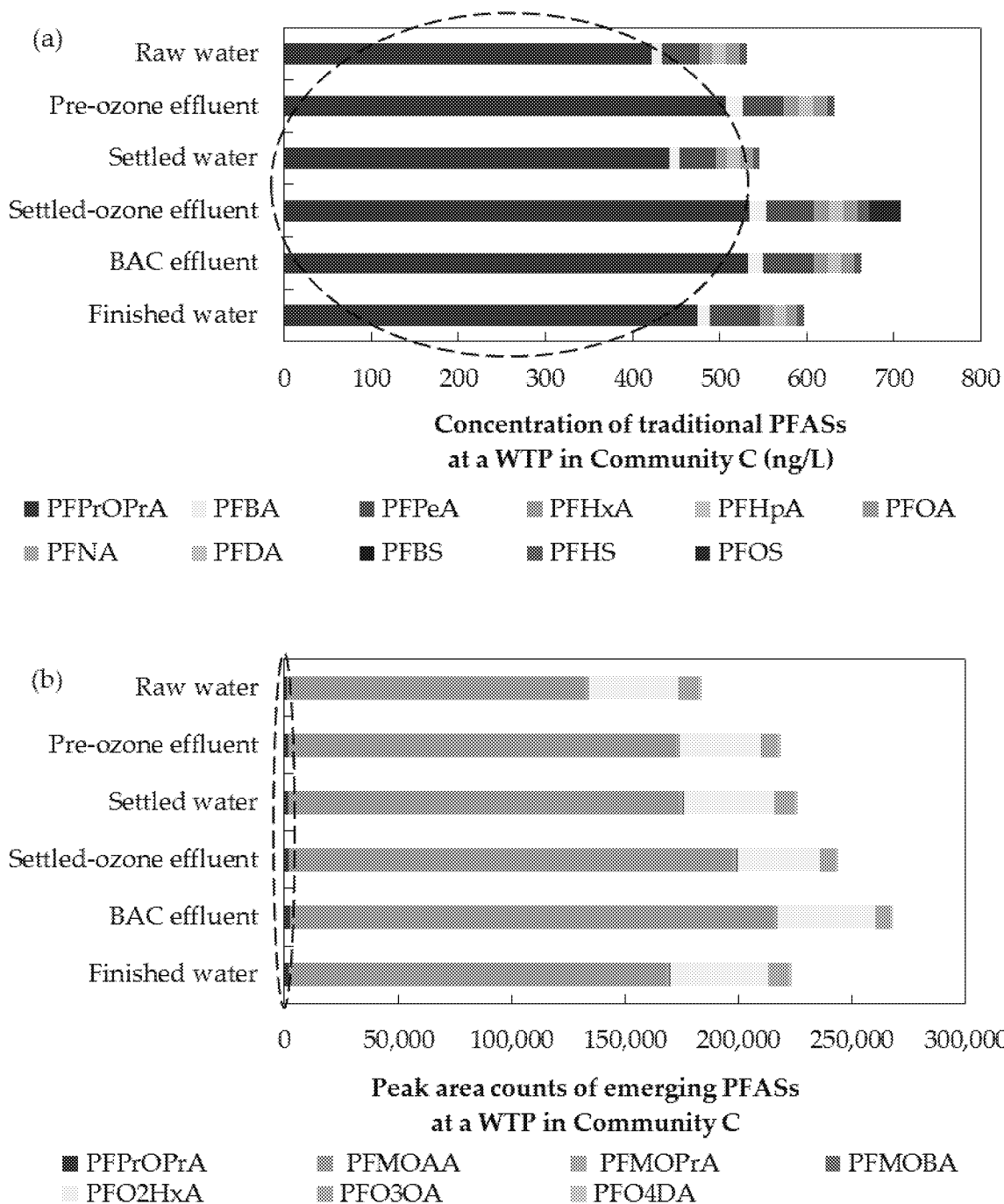   PFO2HxA   ▨ PFO3OA   ▨ PFO4DA

Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for emerging PFECAs, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted in dashed ovals for reference. Compounds with concentrations <QL were not plotted.

191 **PFAS adsorption by PAC**: PAC can effectively remove long-chain PFCAs and PFSAs, but its

192 effectiveness decreases with decreasing PFAS chain length.[24, 25, 29] It is unclear, however, how

193 the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 hour, a

194 PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths

195 ≥7. At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40%

196 for other PFECAs. Detailed removal percentage data as a function of PAC contact time are

197 shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the

198 variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA

199 could not be quantified by the analytical method used for these experiments; however, based on

200 the observations that PFAS adsorption decreases with decreasing carbon chain length and that

201 PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA)

202 exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also

203 negligible at the tested conditions.

204 To compare the affinity of different PFASs for PAC, the PFAS removal percentages in solution

205 were plotted as a function of PFAS chain length (the sum of carbon (including branched), ether

206 oxygen, and sulfur atoms) (Figure 3(b)). The adsorbability of both legacy and emerging PFASs

207 increased with increasing chain length. PFSAs were more readily removed than PFCAs of

208 matching chain length, which agrees with previous studies.[24, 25, 29] PFECAs exhibited lower

209 adsorbabilities than PFCAs of the same chain length (e.g. PFMOBA<PFHxA), suggesting that

210 the replacement of a CF_2 group with an ether oxygen atom decreases the affinity of PFASs for

211 PAC. However, the replacement of additional CF_2 groups with ether groups resulted in small or

212 negligible affinity changes among the studied PFECAs (e.g., PFMOBA~PFO2HxA).

213 Alternatively, if only the number of perfluorinated carbons were considered as a basis of

214 comparing adsorbability, the interpretation would be different. In that case, with the same

215 number of perfluorinated carbons, PFCAs have a higher affinity for PAC than mono-ether

216 PFECAs (e.g., PFPeA>PFMOBA), but a lower affinity than multi-ether PFECAs (e.g.,

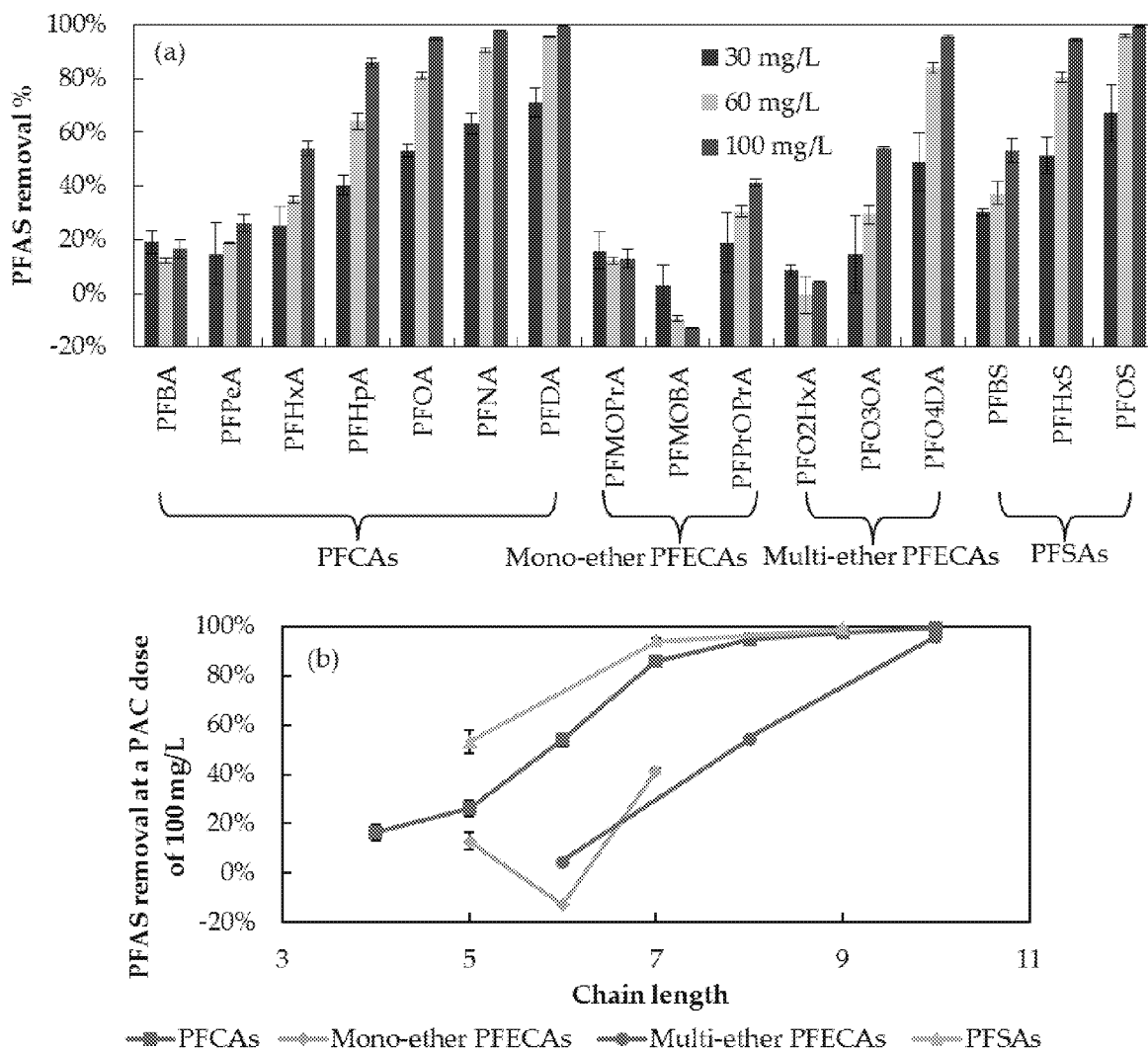217 PFPeA<PFO3OA).

218

219

220 **Figure 3.** PFAS adsorption on PAC (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a

221 function of PFAS chain length. PAC contact time in CFR water was 1 hour. Legacy PFASs were

222 spiked at ~1000 ng/L and the emerging PFASs were at ambient concentrations. Figures show

223 average PFAS removal percentages, and error bars show one standard deviation of replicate

224 experiments.

225

226 To the knowledge of the authors, this is the first paper reporting the behavior of recently

227 identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS

228 signature in a drinking water source downstream of a fluorochemical manufacturer and that

229 PFECA removal by many conventional and advanced treatment processes was negligible. Our

230 adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is

231 replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA.

232 The detection of potentially high levels of PFECAs, the continued presence of high levels of

233 legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many

234 water treatment processes, suggest the need for broader discharge control and contaminant

235 monitoring.

236 **Acknowledgement**

239 **Notes**

240 The views expressed in this article are those of the authors and do not necessarily represent the

241 views or policies of the USEPA.

242 The authors declare no competing financial interest.

243

244 **Supporting Information Available**

245 The following information is available free of charge via the Internet at http://pubs.acs.org: Six

246 tables, five figures, information about PFASs, analytical methods, and detailed results .

247 **Reference**

248 1.   Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaider, L. A.; Grandjean, P.;
249 Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A., *et al.*, Detection of poly- and perfluoroalkyl
250 substances (PFASs) in U.S. drinking water linked to industrial sites, military fire training areas,
251 and wastewater treatment plants. *Environ. Sci. Technol. Lett.* **2016,** *3*, (10), 344–350.
252 2.   Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A.
253 A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J., Perfluoroalkyl and polyfluoroalkyl

254 substances in the environment: Terminology, classification, and origins. *Integr. Enviro. Assess.*
255 *Manage.* **2011,** *7,* (4), 513-541.

256 3.   Kennedy, G. L.; Butenhoff, J. L.; Olsen, G. W.; O'Connor, J. C.; Seacat, A. M.; Perkins, R.
257 G.; Biegel, L. B.; Murphy, S. R.; Farrar, D. G., The toxicology of perfluorooctanoate. *Crit. Rev.*
258 *Toxicol.* **2004,** *34,* (4), 351-384.

259 4.   D. Borg; H. Hakansson *Environmental and health risk assessment of perfluoroalkylated and*
260 *polyfluoroalkylated substances (PFASs) in sweden, Report 6513;* The Swedish Environmental
261 Protention Agency: 2012.

262 5.   US Environmental Protection Agency *Drinking water health advisory for perfluorooctanoic*
263 *acid (PFOA)* 822-R-16-005; 2016.

264 6.   US Environmental Protection Agency *Drinking water health advisory for perfluorooctane*
265 *sulfonate (PFOS)* 822-R-16-004; 2016.

266 7.   Scheringer, M.; Trier, X.; Cousins, I. T.; de Voogt, P.; Fletcher, T.; Wang, Z.; Webster, T.
267 F., Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs). *Chemosphere*
268 **2014,** *114,* 337-339.

269 8.   Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbühler, K., Fluorinated alternatives to
270 long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and
271 their potential precursors. *Environ. Int.* **2013,** *60,* 242-248.

272 9.   Wang, Z.; Cousins, I. T.; Scheringer, M.; Hungerbuehler, K., Hazard assessment of
273 fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status
274 quo, ongoing challenges and possible solutions. *Environ. Int.* **2015,** *75,* 172-179.

275 10.   Barzen-Hanson, K. A.; Field, J. A., Discovery and implications of C2 and C3
276 perfluoroalkyl sulfonates in aqueous film-forming foams and groundwater. *Environ. Sci.*
277 *Technol. Lett.* **2015,** *2,* (4), 95-99.

278 11.   Strynar, M.; Dagnino, S.; McMahen, R.; Liang, S.; Lindstrom, A.; Andersen, E.; McMillan,
279 L.; Thurman, M.; Ferrer, I.; Ball, C., Identification of novel perfluoroalkyl ether carboxylic acids
280 (PFECAs) and sulfonic acids (PFESAs) in natural waters using accurate mass time-of-flight mass
281 spectrometry (TOFMS). *Environ. Sci. Technol.* **2015,** *49,* (19), 11622-11630.

282 12.   Miyake, Y.; Yamashita, N.; Rostkowski, P.; So, M. K.; Taniyasu, S.; Lam, P. K. S.; Kannan,
283 K., Determination of trace levels of total fluorine in water using combustion ion
284 chromatography for fluorine: A mass balance approach to determine individual perfluorinated
285 chemicals in water. *J. Chromatogr. A* **2007,** *1143,* (1–2), 98-104.

286 13.   Wagner, A.; Raue, B.; Brauch, H.-J.; Worch, E.; Lange, F. T., Determination of adsorbable
287 organic fluorine from aqueous environmental samples by adsorption to polystyrene-
288 divinylbenzene based activated carbon and combustion ion chromatography. *J. Chromatogr. A*
289 **2013,** *1295,* 82-89.

290 14.   Willach, S.; Brauch, H.-J.; Lange, F. T., Contribution of selected perfluoroalkyl and
291 polyfluoroalkyl substances to the adsorbable organically bound fluorine in German rivers and
292 in a highly contaminated groundwater. *Chemosphere* **2016,** *145,* 342-350.

293 15.   Heydebreck, F.; Tang, J.; Xie, Z.; Ebinghaus, R., Alternative and legacy perfluoroalkyl
294 substances: Differences between european and chinese river/estuary systems. *Environ. Sci.*
295 *Technol.* **2015,** *49,* (14), 8386-8395.

296   16.   Gannon, S. A.; Fasano, W. J.; Mawn, M. P.; Nabb, D. L.; Buck, R. C.; Buxton, L. W.;
297   Jepson, G. W.; Frame, S. R., Absorption, distribution, metabolism, excretion, and kinetics of
298   2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid ammonium salt following a single
299   dose in rat, mouse, and cynomolgus monkey. *Toxicology* **2016,** *340,* 1-9.
300   17.   Hoke, R. A.; Ferrell, B. D.; Sloman, T. L.; Buck, R. C.; Buxton, L. W., Aquatic hazard,
301   bioaccumulation and screening risk assessment for ammonium 2,3,3,3-tetrafluoro-2-
302   (heptafluoropropoxy)-propanoate. *Chemosphere* **2016,** *149,* 336-342.
303   18.   Caverly Rae, J. M.; Craig, L.; Slone, T. W.; Frame, S. R.; Buxton, L. W.; Kennedy, G. L.,
304   Evaluation of chronic toxicity and carcinogenicity of ammonium 2,3,3,3-tetrafluoro-2-
305   (heptafluoropropoxy)-propanoate in Sprague–Dawley rats. *Toxicol. Rep.* **2015,** *2,* 939-949.
306   19.   Wang, J.; Wang, X.; Sheng, N.; Zhou, X.; Cui, R.; Zhang, H.; Dai, J., RNA-sequencing
307   analysis reveals the hepatotoxic mechanism of perfluoroalkyl alternatives, HFPO2 and HFPO4,
308   following exposure in mice. *J. Appl. Toxicol.* **2016.**
309   20.   Gomis, M. I.; Wang, Z.; Scheringer, M.; Cousins, I. T., A modeling assessment of the
310   physicochemical properties and environmental fate of emerging and novel per- and
311   polyfluoroalkyl substances. *Sci. Total Environ.* **2015,** *505,* 981-991.
312   21.   Rayne, S.; Forest, K., Perfluoroalkyl sulfonic and carboxylic acids: A critical review of
313   physicochemical properties, levels and patterns in waters and wastewaters, and treatment
314   methods. *Journal of Environmental Science and Health, Part A* **2009,** *44,* (12), 1145-1199.
315   22.   Quiñones, O.; Snyder, S. A., Occurrence of perfluoroalkyl carboxylates and sulfonates in
316   drinking water utilities and related waters from the United States. *Environ. Sci. Technol.* **2009,** *43,*
317   (24), 9089-9095.
318   23.   Shivakoti, B. R.; Fujii, S.; Nozoe, M.; Tanaka, S.; Kunacheva, C., Perfluorinated chemicals
319   (PFCs) in water purification plants (WPPs) with advanced treatment processes. *Water Sci.*
320   *Technol. Water Supply* **2010,** *10,* (1), 87-95.
321   24.   Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P., Impact of
322   treatment processes on the removal of perfluoroalkyl acids from the drinking water production
323   chain. *Environ. Sci. Technol.* **2012,** *46,* (3), 1708-1715.
324   25.   Rahman, M. F.; Peldszus, S.; Anderson, W. B., Behaviour and fate of perfluoroalkyl and
325   polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res.* **2014,** *50,*
326   318-340.
327   26.   Appleman, T. D.; Higgins, C. P.; Quiñones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-
328   Holady, J. C.; Dickenson, E. R. V., Treatment of poly- and perfluoroalkyl substances in U.S. full-
329   scale water treatment systems. *Water Res.* **2014,** *51,* 246-255.
330   27.   Merino, N.; Qu, Y.; Deeb, R. A.; Hawley, E. L.; Hoffmann, M. R.; Mahendra, S.,
331   Degradation and removal methods for perfluoroalkyl and polyfluoroalkyl substances in water.
332   *Environ. Eng. Sci.* **2016,** *33,* (9), 615-649.
333   28.   Appleman, T. D.; Dickenson, E. R. V.; Bellona, C.; Higgins, C. P., Nanofiltration and
334   granular activated carbon treatment of perfluoroalkyl acids. *J. Hazard. Mater.* **2013,** *260,* 740-746.
335   29.   Dudley, L. A.; Arevalo, E. C.; Knappe, D. R. U. *Removal of perfluoroalkyl substances by PAC*
336   *adsorption and anion exchange;* Water Research Foundation: Denver, CO, 2015.
337   30.   Dunn, S. E.; Knappe, D. R. U. *Disinfection by-product precursor and micropollutant removal*
338   *by powdered activated carbon;* Water Research Foundation: Denver, CO, 2013.

339   31.   Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A. B.,

340   Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environ. Sci.*

341   *Technol.* **2007,** *41*, (15), 5271-5276.

342   32.   US Environmental Protection Agency Unregulated contaminant monitoring rule 3

343   (UCMR 3). http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/ (accessed July 29, 2016),

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